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Patents Form 1/77

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Request for grant of a patent

1.	Your Reference	RWF/CK/W634
2	0221093.8	12 SEP 2002
3.	Full name, address and postcode of the or each Applicant Country/state of incorporation (if applicable)	**Lucite International UK Limited** **Queens Gate** **15-17 Queens Terrace** **SOUTHAMPTON** **Hampshire** **SO14 3BP** 8432809001 **Incorporated in: UK**
4.	Title of the invention	**METALLOCENE CATALYST**
5.	Name of agent Address for service in the UK to which all correspondence should be sent Patents ADP number	**APPLEYARD LEES** **15 CLARE ROAD** **HALIFAX** **HX1 2HY** **190001**
6.	Priority claimed to:	Country / Application number / Date of filing
7.	Divisional status claimed from:	Number of parent application: - / Date of filing: -
8.	Is a statement of inventorship and of right to grant a patent required in support of this application?	**YES**

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document	
Continuation sheets of this form	
Description	51
Claim(s)	8
Abstract	1
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Priority documents	
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Statement of inventorship and right to grant a patent (PF 7/77)	
Request for a preliminary examination and search (PF 9/77)	ONE
Request for substantive examination (PF 10/77)	
Any other documents (please specify)	

11. We request the grant of a patent on the basis of this application.

Signature Date

APPLEYARD LEES **11/9/02**

Appleyard Lees.

12. Contact **Richard W Frith- 01422 330110**

DUPLICATE

METALLOCENE CATALYST

The present invention relates to compounds, in particular compounds for catalysing the carbonylation of ethylenically unsaturated compounds, methods of preparing such compounds and the use of such compounds for catalysing the carbonylation of ethylenically unsaturated compounds.

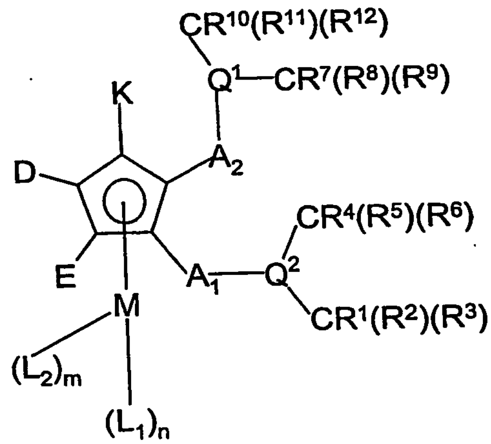
The carbonylation of ethylenically unsaturated compounds using carbon monoxide in the presence of a catalyst system and an alcohol or water to yield the corresponding ester or carboxylic acid, respectively, is well known. Suitable catalyst systems comprise a Group VIII metal (e.g. palladium) and a phosphine ligand (e.g. an alkyl phosphine or a bidentate phosphine ligand as disclosed in WO-A-9619434).

Although catalyst systems have been developed which exhibit reasonable stability during the carbonylation process and permit relatively high reaction rates to be achieved, there still exists a need for improved catalyst systems. Suitably, the present invention aims to provide an improved catalyst for carbonylating ethylenically unsaturated compounds.

According to a first aspect, the present invention provides a catalyst suitable for carbonylating an ethylenically unsaturated compound, which catalyst is obtainable by combining:

(a) a Group VIIIB metal or a compound thereof; and,

(b) a compound of formula I



(I)

wherein:

A_1 and A_2, and A_3, A_4 and A_5 (when present), each independently represent lower alkylene;

K is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29}, $C(O)SR^{30}$, or $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$;

D is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29}, $C(O)SR^{30}$, or $-A_4-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$;

E is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29}, $C(O)SR^{30}$, or $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$;

or both D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form a phenyl ring, which is optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29} or $C(O)SR^{30}$;

R^1 to R^{18} and R^{31} to R^{42} each independently represent lower alkyl, aryl, or Het;

Q^1 and Q^2, and Q^3, Q^4 and Q^5 (when present), each independently represent phosphorus, arsenic or antimony;

M represents a Group VIB or VIIIB metal or metal cation thereof;

L_1 represents a cyclopentadienyl, indenyl or aryl group each of which groups are optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29}, $C(O)SR^{30}$ or ferrocenyl;

L_2 represents one or more ligands each of which are independently selected from hydrogen, lower alkyl, alkylaryl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$;

R^{19} to R^{30} and R^{43} to R^{48} each independently represent hydrogen, lower alkyl, aryl or Het;

$n = 0$ or 1;

and $m = 0$ to 5;

provided that when n = 1 then m equals 0, and when n equals 0 then m does not equal 0;

provided that when both K represents $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and E represents $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$, then D represents $-A_4-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$.

Such compounds are referred to hereinafter as "the compounds of the invention".

Suitably, the compounds of the invention may catalyse the carbonylation of an ethylenically unsaturated compound in the presence of carbon monoxide and a hydroxyl group containing compound i.e. the compounds of the invention may catalyse the conversion of an ethylenically unsaturated compound to the corresponding carboxylic acid or ester, respectively, depending on the choice of hydroxyl group containing compound used. Conveniently, the compounds of the invention may exhibit a high stability under typical carbonylation reaction conditions such that they require little or no replenishment. Conveniently, the compounds of the invention may increase the rate of the carbonylation reaction of an ethylenically unsaturated compound compared to known catalysts. Conveniently, the compounds of the invention may promote high conversion rates of the ethylenically unsaturated compound, thereby yielding the desired product in high yield with little or no impurities. Consequently, employing the compounds of the invention may increase the commercial viability of a carbonylation process, such as the carbonylation of an ethylenically unsaturated compound.

The term "aryl" when used herein, includes six-to-ten-membered carbocyclic aromatic groups, such as phenyl and naphthyl, which groups are optionally substituted with one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below), Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29}, $C(O)SR^{30}$ or $C(S)NR^{27}R^{28}$ wherein R^{19} to R^{30} each independently represent hydrogen, aryl or lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below).

The term "Het", when used herein, includes four-to-twelve-membered, preferably four-to-ten-membered ring systems, which rings contain one or more heteroatoms selected from nitrogen, oxygen, sulfur and mixtures thereof, and which rings contain one or more double bonds or be non-aromatic, partly aromatic or wholly aromatic in character. The ring systems may be monocyclic, bicyclic or fused. Each "Het" group identified herein is optionally substituted by one or more substituents selected from halo, cyano, nitro, oxo, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below) OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29}, $C(O)SR^{30}$ or $C(S)NR^{27}R^{28}$ wherein R^{19} to R^{30} each independently represent hydrogen, aryl or lower alkyl (which alkyl group itself may be optionally substituted or terminated as defined below). The term "Het" thus includes groups such as optionally substituted azetidinyl, pyrrolidinyl, imidazolyl, indolyl, furanyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, thiadiazolyl, triazolyl, oxatriazolyl, thiatriazolyl, pyridazinyl, morpholinyl, pyrimidinyl, pyrazinyl, quinolinyl, isoquinolinyl,

piperidinyl, pyrazolyl and piperazinyl. Substitution at Het may be at a carbon atom of the Het ring or, where appropriate, at one or more of the heteroatoms.

"Het" groups may also be in the form of an N oxide.

The term "lower alkyl" when used herein, means C_1 to C_{10} alkyl and includes methyl, ethyl, propyl, butyl, pentyl, hexyl and heptyl groups. Unless otherwise specified, alkyl groups may, when there is a sufficient number of carbon atoms, be linear or branched, be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, and/or be substituted or terminated by one or more substituents selected from halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29}, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl or Het, wherein R^{19} to R^{30} each independently represent hydrogen, aryl or lower alkyl, and/or be interrupted by one or more oxygen or sulfur atoms, or by silano or dialkylsilcon groups.

Lower alkyl groups which R^1 to R^{48}, K, D, E and L_2 may represent and which aryl, Het and L_1 may be substituted, may, when there is a sufficient number of carbon atoms, be linear or branched, be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, and/or be interrupted by one or more of oxygen or sulfur atoms, or by silano or dialkylsilicon groups, and/or be substituted by one or more substituents selected from halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29}, $C(O)SR^{30}$, $C(S)NR^{27}R^{28}$, aryl or Het wherein R^{19} to R^{30} each independently represent hydrogen, aryl or lower alkyl.

Similarly, the term "lower alkylene" which A_1 and A_2, and A_3, A_4 and A_5 (when present), represent in a compound of formula I, when used herein, includes C_1 to C_{10} groups which can be bonded at two places on the group and is otherwise defined in the same way as "lower alkyl".

Suitably, when D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form a phenyl ring, the metal M or cation thereof is attached to an indenyl ring system.

By the term "M represents a Group VIB or VIIIB metal" in a compound of formula I we include metals such as Cr, Mo, W, Fe, Co, Ni, Ru and Rh.

By the term "metal cation thereof" we mean that the Group VIB or VIIIB metal (M) in the compound of formula I as defined herein has a positive charge. Suitably, the metal cation may be in the form of a salt or may comprise weakly coordinated anions derived from halo, nitric acid; sulphuric acid; lower alkanoic (up to C_{12}) acids such as acetic acid and propionic acid; sulphonic acids such as methane sulphonic acid, chlorosulphonic acid, fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid; sulphonated ion exchange resins; perhalic acid such as perchloric acid; perfluororated carboxylic acid such as trichloroacetic acid and trifluoroacetic acid; orthophosphoric acid; phosphonic acid such as benzene phosphonic acid; and acids derived from interactions between Lewis acids and Broensted acids. Other sources

which may provide suitable anions include the tetraphenyl borate derivatives.

Preferably M represents a Group VIB or VIIIB metal. In other words the total electron count for the metal M is 18.

Halo groups, which L_2 may represent and with which the above-mentioned groups may be substituted or terminated, include fluoro, chloro, bromo and iodo.

Where a compound of the formula (I) contains an alkenyl group, cis (E) and trans (Z) isomerism may also occur. The present invention includes the individual stereoisomers of the compounds of formula (I) and, where appropriate, the individual tautomeric forms thereof, together with mixtures thereof. Separation of diastereoisomers or cis and trans isomers may be achieved by conventional techniques, e.g. by fractional crystallisation, chromatography or H.P.L.C. of a stereoisomeric mixture of a compound of the formula (I) or a suitable salt or derivative thereof. An individual enantiomer of a compound of the formula (I) may also be prepared from a corresponding optically pure intermediate or by resolution, such as by H.P.L.C. of the corresponding racemate using a suitable chiral support or by fractional crystallisation of the diastereoisomeric salts formed by reaction of the corresponding racemate with a suitable optically active acid or base, as appropriate.

All stereoisomers are included within the scope of the invention.

Suitable Group VIIIB metals or a compound thereof which may be combined with a compound of formula I thereby forming the compounds of the invention include cobalt, nickel, palladium, rhodium and platinum. Preferably, the Group VIIIB metal is palladium or a compound thereof. Suitable compounds of such Group VIIIB metals include salts of such metals with, or compounds comprising weakly coordinated anions derived from, nitric acid; sulphuric acid; lower alkanoic (up to C_{12}) acids such as acetic acid and propionic acid; sulphonic acids such as methane sulphonic acid, chlorosulphonic acid, fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid; sulphonated ion exchange resins; perhalic acid such as perchloric acid; perfluororated carboxylic acid such as trichloroacetic acid and trifluoroacetic acid; orthophosphoric acid; phosphonic acid such as benzene phosphonic acid; and acids derived from interactions between Lewis acids and Broensted acids. Other sources, which may provide suitable anions, include the tetraphenyl borate derivatives. Additionally, zero valent palladium with labile ligands e.g. tri(dibenzylideneacetone)dipalladium may be used. Preferably, zero valent Group VIIIB metals with labile ligands are employed.

Suitably, the compounds of the invention when employed to catalyse the carbonylation of ethylenically unsaturated compounds include a source of anions. Conveniently, the source of anions may be derived by combining a Group VIIIB compound thereof as described in the preceding paragraph with a compound of formula I. Alternatively, or

additionally, a separate source of anions as mentioned above may be added to the compounds of the present invention. Preferably, the source of anions are derived from an acid having a pKa less than 4, more preferably a pKa less than 3, as measured at 18°C in an aqueous solution.

It will be appreciated by those skilled in the art that the compounds of formula I (referred to as (b) above) may function as ligands that coordinate with the Group VIIIB metal or compound thereof (referred to as (a) above) to form the compounds of the invention. Typically, the Group VIIIB metal or compound thereof (a) coordinates to the one or more phosphorus, arsenic and/or antimony atoms of the compound of formula I. It will be appreciated that the compounds of formula I may be referred to broadly as "metallocenes".

Suitably, when n = 1, the compounds of formula I may contain either two cyclopentadienyl rings, two indenyl rings or one indenyl and one cyclopentadienyl ring (each of which ring systems may optionally be substituted as described herein). Such compounds may be referred to as "sandwich compounds" as the metal M or metal cation thereof is sandwiched by the two ring systems. The respective cyclopentadienyl and/or indenyl ring systems may be substantially coplanar with respect to each other or they may be tilted with respect to each other (commonly referred to as bent metallocenes).

Alternatively, when n = 1, the compounds of the invention may contain either one cyclopentadienyl or one indenyl ring (each of which ring systems may optionally be

substituted as described herein) and one aryl ring (i.e. L_1 represents aryl) which is optionally substituted as defined herein. Suitably, when n = 1 and L_1 represents aryl then the metal M of the compounds of formula I as defined herein is typically in the form of the metal cation.

Suitably, when n = 0, the compounds of the invention contain only one cyclopentadienyl or indenyl ring (each of which ring systems may optionally be substituted as described herein). Such compounds may be referred to as "half sandwich compounds". Preferably, when n = 0 then m represents 1 to 5 so that the metal M of the compounds of formula I has an 18 electron count. In other words, when metal M of the compounds of formula I is iron, the total number of electrons contributed by the ligands L_2 is typically five.

Suitably, the metal M or metal cation thereof in the compounds of formula I is typically bonded to the cyclopentadienyl ring(s) or the cyclopentadienyl moiety of the indenyl ring(s). Typically, the cyclopentadienyl ring or the cyclopentadienyl moiety of the indenyl ring exhibits a pentahapto bonding mode with the metal; however other bonding modes between the cyclopentadienyl ring or cyclopentadienyl moiety of the indenyl ring and the metal, such as trihapto coordination, are also embraced by the scope of the present invention.

Preferably, R^1 to R^{18} and R^{31} to R^{42} each independently represent lower alkyl or aryl. More preferably, R^1 to R^{18} and R^{31} to R^{42} each independently represent C_1 to C_6 alkyl, C_1-C_6 alkyl phenyl (wherein the phenyl group is optionally

substituted as defined herein) or phenyl (wherein the phenyl group is optionally substituted as defined herein). Even more preferably, R^1 to R^{18} and R^{31} to R^{42} each independently represent C_1 to C_6 alkyl, which is optionally substituted as defined herein. Most preferably, R^1 to R^{18} and R^{31} to R^{42} each independently represent non-substituted C_1 to C_6 alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.

Alternatively, or additionally, the groups R^1 to R^3, R^4 to R^6, R^7 to R^9, R^{10} to R^{12}, R^{13} to R^{15}, R^{16} to R^{18}, R^{31} to R^{33}, R^{34} to R^{36}, R^{37} to R^{39} or R^{40} to R^{42} together independently may form cyclic structures such as 1-norbornyl or 1-norbornadienyl.

In a particularly preferred embodiment of the present invention R^1, R^4, R^7 and R^{10}, and R^{13}, R^{16}, R^{31}, R^{34}, R^{37} and R^{40} (when present), each represent the same lower alkyl, aryl or Het moiety as defined herein; R^2, R^5, R^8 and R^{11}, and R^{14}, R^{17}, R^{32}, R^{35}, R^{38} and R^{41} (when present), each represent the same lower alkyl, aryl or Het moiety as defined herein; and R^3, R^6, R^9 and R^{12}, and R^{15}, R^{18}, R^{33}, R^{36}, R^{39} and R^{42} (when present), each represent the same lower alkyl, aryl or Het moiety as defined herein. More preferably R^1, R^4, R^7 and R^{10}, and R^{13}, R^{16}, R^{31}, R^{34}, R^{37} and R^{40} (when present) each represent the same C_1-C_6 alkyl, particularly non-substituted C_1-C_6 alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl or cyclohexyl; R^2, R^5, R^8 and R^{11}, R^{14}, R^{17}, R^{32}, R^{35}, R^{38} and R^{41} (when present), each independently represent the same C_1-C_6 alkyl as defined above; and R^3, R^6, R^9 and R^{12}, and R^{15}, R^{18}, R^{33}, R^{36}, R^{39} and R^{42} (when

present), each independently represent the same C_1-C_6 alkyl as defined above. For example: R^1, R^4, R^7, R^{10}, R^{13} and R^{16} each represent methyl; R^2, R^5, R^8, R^{11}, R^{14} and R^{17} each represent ethyl; and, R^3, R^6, R^9, R^{12}, R^{15} and R^{18} each represent n-butyl or n-pentyl.

In an especially preferred embodiment of the present invention each R^1 to R^{18} and R^{31} to R^{42} group represents the same lower alkyl, aryl, or Het moiety as defined herein. Preferably, each R^1 to R^{18} and R^{31} to R^{42} group represents the same C_1 to C_6 alkyl group, particularly non-substituted C_1-C_6 alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl. Most preferably, each R^1 to R^{18} and R^{31} to R^{42} group represents methyl.

In the compound of formula I, preferably each Q^1 and Q^2, and Q^3, Q^4 and Q^5 (when present) are the same. Most preferably, each Q^1 and Q^2, and Q^3, Q^4 and Q^5 (when present), represents phosphorus.

Preferably, in the compound of formula I, A_1 and A_2, and A_3, A_4 and A_5 (when present), each independently represent C_1 to C_6 alkylene which is optionally substituted as defined herein, for example with lower alkyl groups. Preferably, the lower alkylene groups which A_1 to A_5 may represent are non-substituted. A particular preferred lower alkylene, which A_1 to A_5 may independently represent, is $-CH_2-$ or $-C_2H_4-$. Most preferably, each of A_1 and A_2, and A_3, A_4 and A_5 (when present), represent the same lower alkylene as defined herein, particularly $-CH_2-$.

Preferably, in the compound of formula I when K does not represent $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$, K represents hydrogen, lower alkyl, phenyl or lower alkylphenyl. More preferably, K represents hydrogen, phenyl, C_1-C_6 alkylphenyl or C_1-C_6 alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl. Most preferably, K represents hydrogen.

Preferably, in the compound of formula I when D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached do not form a phenyl ring, and when D does not represent $-A_4-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$ and E does not represent $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$, D and E each independently represent hydrogen, lower alkyl, phenyl or lower alkylphenyl. More preferably, D and E each independently represent hydrogen, phenyl, C_1-C_6 alkylphenyl or C_1-C_6 alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl. Even more preferably, both D and E represent the same substituent. Most preferably, both D and E represent hydrogen.

Preferably, in the compound of formula I when K does not represent $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached do not form a phenyl ring, and when E does not represent $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$, each of K, D and E represent the same group selected from hydrogen, lower alkyl, aryl, or Het as defined herein; particularly hydrogen or C_1-C_6 alkyl (more particularly unsubstituted C_1-C_6 alkyl), especially hydrogen.

Preferably, in the compound of formula I when D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form a phenyl ring, then the phenyl ring is optionally substituted with one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below), Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{29}, $C(O)SR^{30}$ or $C(S)NR^{27}R^{28}$ wherein R^{19} to R^{30} each independently represent hydrogen or lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined herein). More preferably, the phenyl ring is not substituted by any substituents i.e. it bears hydrogen atoms only.

Preferably, in the compound of formula I, M represents Cr, Mo, Fe, Co or Ru, or a metal cation thereof. Even more preferably, M represents Cr, Fe, Co or Ru or a metal cation thereof. Most preferably, M is selected from a Group VIIIB metal or metal cation thereof. An especially preferred Group VIIIB metal is Fe. Although the metal M as defined herein may be in a cationic form, preferably it carries essentially no residual charge due to coordination with L_1 and/or L_2 as defined herein.

Preferably, when n = 1 in the compound of formula I, L_1 represents cyclopentadienyl, indenyl or aryl each of which rings are optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, SR^{29} or ferrocenyl (by which we mean the cyclopentadienyl, indenyl or aryl ring which L_1 may represent is bonded directly to the cyclopentadienyl ring of the ferrocenyl group). More preferably, if the cyclopentadienyl, indenyl or aryl ring

which L_1 may represent is substituted it is preferably substituted with one or more substituents selected from C_1-C_6 alkyl, halo, cyano, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$ where R^{19}, R^{20}, R^{21}, R^{22}, R^{23} and R^{24} each independently represent hydrogen or C_1-C_6 alkyl.

Preferably, when n = 1, L_1 represents cyclopentadienyl, indenyl, phenyl or napthyl optionally substituted as defined herein. Preferably, the cyclopentadienyl, indenyl, phenyl or napthyl groups are unsubstituted. More preferably, L_1 represents cyclopentadienyl, indenyl or phenyl, each of which rings are unsubstituted. Most preferably, L_1 represents unsubstituted cyclopentadienyl.

In a particularly preferred embodiment of the present invention, in a compound of formula I, n = 1, L_1 is as defined herein and m = 0.

Alternatively, when n is equal to zero and m is not equal to zero in a compound of formula I, L_2 represents one or more ligands each of which are independently selected from lower alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$. More preferably, L_2 represents one or more ligands each of which are independently selected from C_1 to C_4 alkyl, halo, particularly chloro, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$, wherein R^{43} to R^{48} are independently selected from hydrogen, C_1 to C_6 alkyl or aryl, such as phenyl.

In a particularly preferred alternative embodiment of the present invention, in a compound of formula I, n = 0, L_2 is as defined herein and m = 3 or 4, particularly 3.

Preferred compounds of formula I include those wherein:

A_1 and A_2 each independently represent unsubstituted C_1 to C_6 alkylene;

K is selected from the group consisting of hydrogen, C_1-C_6 alkyl, phenyl, C_1-C_6 alkylphenyl or $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ where Q^3 represents unsubstituted C_1 to C_6 alkylene;

D is selected from the group consisting of hydrogen, C_1-C_6 alkyl, phenyl, C_1-C_6 alkylphenyl or $-A_4-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$;

E is selected from the group consisting of hydrogen, C_1-C_6 alkyl, phenyl, C_1-C_6 alkylphenyl or $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$;

or both D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form a phenyl ring which is optionally substituted by one or more substituents selected from lower alkyl, phenyl or lower alkylphenyl;

R^1 to R^{18} and R^{31} to R^{42} each independently represent C_1 to C_6 alkyl, phenyl or C_1 to C_6 alkylphenyl;

M represents a metal selected from Cr, Mo, Fe, Co or Ru or a metal cation thereof;

L_1 represents cyclopentadienyl, indenyl, napthyl or phenyl, each of which rings may be optionally substituted by one or more substituents selected from C_1-C_6 alkyl, halo, cyano, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)R^{22}$, $NR^{23}R^{24}$;

L_2 represents one or more ligands each of which ligands are independently selected from C_1-C_6 alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$;

n = 0 or 1;
and m = 0 to 4;
provided that when n = 1 then m = 0 and when m does not equal zero then n = 0.

Further preferred compounds of formula I include those wherein:

A_1 and A_2 both represent $-CH_2-$ or C_2H_4, particularly CH_2;

K is selected from the group consisting of hydrogen, C_1-C_6 alkyl, C_1-C_6 alkylphenyl, or $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ where A_3 is the same as A_1;

D is selected from the group consisting of hydrogen, C_1-C_6 alkylphenyl, C_1-C_6 alkyl or $-A_4-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$ where A_4 is the same as A_1;

E is selected from the group consisting of hydrogen, C_1-C_6 alkylphenyl, C_1-C_6 alkyl or $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$ where A_5 is the same as A_1;

or both D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;

R^1 to R^{18} and R^{31} to R^{42} each independently represent C_1 to C_6 alkyl;

M represents iron or a cation thereof;

L_1 represents cyclopentadienyl, indenyl or phenyl group, each of which groups are optionally substituted by one or more substituents selected from C_1-C_6 alkyl, halo, cyano, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)R^{22}$;

L_2 represents one or more ligands each of which are independently selected from C_1-C_6 alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$, where R^{43} to R^{48} are independently selected from hydrogen, C_1-C_6 alkyl or phenyl;

$n = 0$ or 1; and $m = 0$ to 4.

Still further preferred compounds of formula I include those wherein:

R^1 to R^{18} and R^{31} to R^{42} are the same and each represents C_1 to C_6 alkyl, particularly methyl.

Still further preferred compounds of formula I include those wherein:

K, D and E are each independently selected from the group consisting of hydrogen or C_1 to C_6 alkyl, particularly where each of K, D and E represent the same group, especially where each of K, D and E represent hydrogen; or

K represents $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and D and E are each independently selected from the group consisting of hydrogen or C_1 to C_6 alkyl, particularly where both D

and E represent the same group, especially where both D and E represent hydrogen; or

E represents $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$ and K and D are each independently selected from the group consisting of hydrogen or C_1 to C_6 alkyl, particularly where both D and K represent the same group, especially where both D and K represent hydrogen; or

K represents $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$, D represents $A_4-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$ and E represents $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$.

Still further preferred compounds of formula I include those wherein:

L_1 represents unsubstituted cyclopendadienyl, indenyl or phenyl, particularly unsubstituted cyclopentadienyl; and, $n = 1$ and $m = 0$.

Alternative preferred compounds of formula I include those wherein:

$n = 0$;

L_2 represents one or more ligands each of which are independently selected from C_1 to C_6 alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$, where R^{43} to R^{48} are independently selected from hydrogen, C_1-C_6 alkyl or phenyl; and $m = 1$ to 4, particularly 3 or 4. For example, when m=3 the three ligands which L_2 may represent include $(CO)_2$halo, $(PR^{43}R^{44}R^{45})_2$halo or $(NR^{46}R^{47}R^{48})_2$halo.

Especially preferred specific compounds of formula I include those wherein:

(1) each of R^1 to R^{12} is the same and represents C_1-C_6 alkyl, particularly methyl;
A_1 and A_2 are the same and represent $-CH_2-$;
K, D and E are the same and represent hydrogen or C_1-C_6 alkyl, particularly hydrogen;
Q^1 and Q^2 both represent phosphorus;
M represents Fe;
n = 1 and L_1 represents cyclopentadienyl, and m = 0.

(2) each of R^1 to R^{18} are the same and represents C_1-C_6 alkyl, particularly methyl;
A_1 and A_2 are the same and represent $-CH_2-$;
K represents $-CH_2-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$;
Q^1, Q^2 and Q^3 each represent phosphorus;
D and E are the same and represent hydrogen or C_1-C_6 alkyl, particularly hydrogen;
M represents Fe;
n = 1 and L_1 represents cyclopentadienyl, and m = 0.

(3) each of R^1 to R^{18} are the same and represents C_1-C_6 alkyl, particularly methyl;
A_1 and A_2 are the same and represent $-CH_2-$;
K represents $-CH_2-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$;
Q^1, Q^2 and Q^3 each represent phosphorus;
D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;
M represents Fe;
n = 1 and L_1 represents cyclopentadienyl, and m = 0.

(4) each of R^1 to R^{12} is the same and represents C_1-C_6 alkyl, particularly methyl;

A_1 and A_2 are the same and represent $-CH_2-$;

Q^1 and Q^2 both represent phosphorus;

K represents hydrogen or C_1-C_6 alkyl, particularly hydrogen;

D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;

M represents Fe;

n = 1 and L_1 represents cyclopentadienyl, and m = 0.

(5) each of R^1 to R^{12} and R^{37} to R^{42} are the same and represents C_1-C_6 alkyl, particularly methyl;

A_1 and A_2 are the same and represent $-CH_2-$;

E represents $-CH_2-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$;

Q^1, Q^2 and Q^5 each represent phosphorus;

D and K are the same and represent hydrogen or C_1-C_6 alkyl, particularly hydrogen;

M represents Fe;

n = 1 and L_1 represents cyclopentadienyl, and m = 0.

(6) each of R^1 to R^{18} and R^{31} to R^{42} are the same and represents C_1-C_6 alkyl, particularly methyl;

A_1 and A_2 are the same and represent $-CH_2-$;

K represents $-CH_2-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$;

D represents $-CH_2-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$;

E represents $-CH_2-Q^5(CR^{37}(R^{38})(R^{39})CR^{40}(R^{41})(R^{42})$;

Q^1, Q^2, Q^3, Q^4 and Q^5 each represent phosphorus

M represents Fe;

n = 1 and L_1 represents cyclopentadienyl; and m = 0.

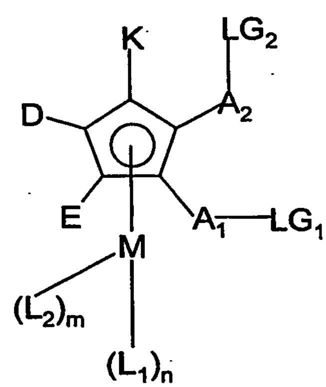
According to a second aspect, the present invention provides a process for preparing the compounds of the invention comprising combining (a) a Group VIIIB metal or compound thereof, as defined herein; with (b) a compound of formula I as defined herein. Conveniently, the compounds of the invention may be obtained by dissolving the Group VIIIB metal or compound thereof as defined herein in a suitable solvent such as the ultimate end product of the carbonylation reaction, for example methylpropanoate where the ethylenically unsaturated compound to be carbonylated is ethene in the presence of methanol or methylnonanoate where it is intended to carbonylate octene in the presence of methanol. Preferably, the reactants are mixed at room temperature under an inert atmosphere (e.g. under nitrogen). The molar ratio of the compound of formula I (referred to as (b)) to the Group VIIIB metal or compound thereof (referred to as (a)) is preferably in the range of 1:1 to 5:1, more preferably in the range of 1:1 to 3:1, most preferably in the range of 1:1 to 1:1.25. Conveniently, the possibility of applying these low molar ratios is advantageous, as it avoids the use of an excess of the compound of formula I and hence minimises the consumption of these usually expensive compounds. Suitably, the compounds of the invention are prepared in a separate step preceding their use in-situ in the carbonylation reaction of an ethylenically unsaturated compound. As mentioned previously, the compounds of the invention may include additional anions derivable from the Group VIIIB compound thereof, if one is employed, and/or by the addition of a separate source of anions. If a separate source of anions is employed these may be added to the compounds of the invention prior to use in the carbonylation reaction.

Alternatively, or additionally, a separate source of anions may be added to the carbonylation reaction.

According to a third aspect, the present invention provides a compound of formula I as defined herein.

According to a fourth aspect, the present invention provides a process for the preparation of the compounds of formula I, which comprises the reaction of a compound of formula II wherein A_1, A_2, K, D, E, M, L_1, L_2, n and m are as defined for a compound of formula I, and LG_1 and LG_2 represent suitable leaving groups,

with a compound of formula IIIa and IIIb



(II)

$HQ^2(CR^1(R^2)(R^3))CR^4(R^5)(R^6)$ (IIIa)

$HQ^1(CR^7(R^8)(R^9))CR^{10}(R^{11})(R^{12})$ (IIIb)

wherein R^1 to R^{12}, Q^1 and Q^2 are as defined for a compound of formula I.

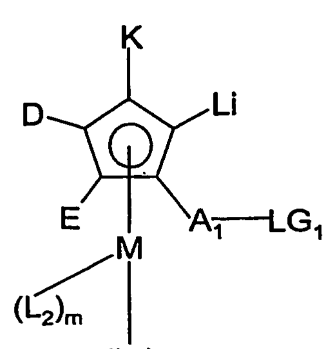
Suitable leaving groups which LG_1 and LG_2 may independently represent include groups which are readily displaced by nucleophilic attack by the phosphine , arsine

or stibene derivatives IIIa and IIIb. Examples of such groups include halo, particularly bromo and iodo, $-NR^{23}R^{24}$ where R^{23} and R^{24} both represent lower alkyl, particularly methyl, and hyroxyl whether in a protonated form or not. Preferably, LG_1 and LG_2 each independently represent $-NMe_2$ or hydroxyl. Most preferably, both LG_1 and LG_2 represent $-NMe_2$, or LG_1 and LG_2 represent NMe_2 or hydroxyl, respectively.

The reaction may be accomplished using methods which are well known to those skilled in the art. For example, the reaction may be accomplished by heating a solution of a compound of formula II with a compound of formula IIIa and IIIb in anhydrous acetic acid at a temperature between 70 to 90°C, preferably approximately 80°C under an inert atmosphere, such as a nitrogen atmosphere.

Preferably, in the compounds of formula IIIa and IIIb, Q^1 is the same as Q^2, R^1 is the same as R^7, R^2 is the same as R^8, R^3 is the same as R^9, R^4 is the same as R^{10}, R^5 is the same as R^{11}, and R^6 is the same as R^{12}.

A compound of formula II, where LG_2 represents hydroxyl or $NR^{23}R^{24}$, may be prepared by reaction of a compound of formula IV, wherein A_1, LG_1, K, D, E, M, L_1, L_2, n and m are as defined for a compound of formula II, and Li represents lithium,



with a compound of formula Va

$$A_2{=}LG_2$$
(Va)

wherein A_2 is as defined for a compound of formula II and LG_2 represents oxygen (thereby forming a hydroxyl derivative following reaction with compound IV) or $NR^{23}R^{24}$.

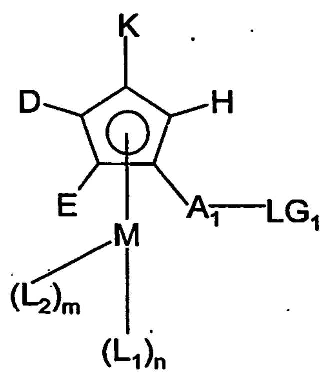
Preferably, in a compound of formula Va, A_2 represents methylene and LG_2 represents NMe_2. For example, a compound of formula Va may represent Eschenmosers salt $I^-CH_2N^+Me_2$ (see Glidewell C, Journal of Organometallic Chemistry, 527, (1997), p.259-261).

Alternatively, in a compound of formula Va, A_2 represents methylene and LG_2 represents oxygen. For example, a compound of formula Va may represent formaldehyde, which for practical purposes may be paraformaldehyde.

The reaction may be carried out using methods which are well known to those skilled in the art. For example, the reaction may be accomplished by stirring a solution of the compound of formula IV and Va in an appropriate solvent, such as diethyl ether, at room temperature.

Preferably, in a compound of formula IV, LG_1 does not represent hydroxyl, as the hydroxyl functionality will typically have to be protected prior to ortho-lithiating the precursor compound (compound VI below) to the compound of formula IV. Preferably, in a compound of formula IV, LG_1 represents $NR^{23}R^{24}$, most preferably LG_1 represents NMe_2.

A compound of formula IV may be prepared by ortho-lithiation of a compound of formula VI, wherein A_1, LG_1, K, D, E, M, L_1, L_2, n and m are as defined for a compound of formula IV,

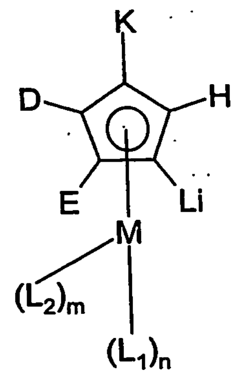


(VI)

by reaction with an alkyl lithium (e.g. n-butyl lithium). Preferably, in a compound of formula VI, LG_1 does not represent hydroxyl, as the hydroxyl functionality will typically have to be protected prior to performing the ortho-lithiation reaction. Preferably, in a compound of formula VI, LG_1 represents $NR^{23}R^{24}$, most preferably LG_1 represents NMe_2.

Typically, the ortho-lithiation reaction of compounds of formula VI with an alkyl lithium is performed in an inert solvent, for example tetrahydrofuran or hexane, at low temperatures (e.g. -78°C), under a nitrogen atmosphere.

A compound of formula VI, where LG_1 represents hydroxyl or $NR^{23}R^{24}$, may be prepared from a compound of formula VII wherein K, D, E, M, L_1, L_2, n and m are as defined for a compound of formula VI and Li represents lithium



(VII)

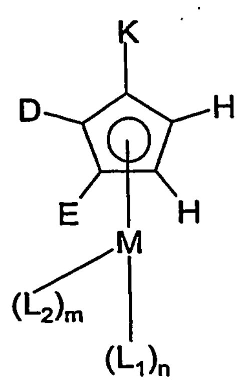
by reaction with a compound of formula Vb

$$A_1{=}LG_1$$

(Vb)

wherein A_1 is as defined for a compound of formula VI and LG_1 represents oxygen (thereby forming a hydroxyl derivative following reaction with compound VII) or $NR^{23}R^{24}$. Preferably, LG_1 represents $NR^{23}R^{24}$, especially NMe_2. In other words, a compound of formula Vb is preferably Eschenmosers salt. The reaction may be accomplished using similar conditions as described for the preparation of a compound of formula II above.

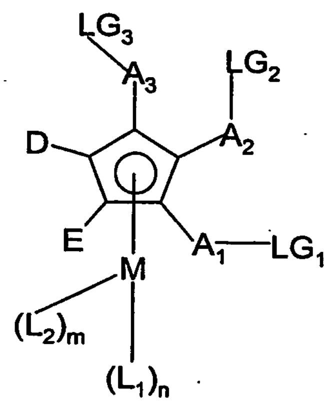
Similarly, a compound of formula VII may be prepared by lithiation of a compound of formula VIII



(VIII)

wherein K, D, E, M, L_1, L_2, n and m are as defined for a compound of formula VII.

Suitably, a compound of formula I wherein K represents $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ may be prepared from a compound of formula IX wherein A_1, A_2, A_3, D, E, M, L_1, L_2, n and m are as defined for a compound of formula I, and LG_1, LG_2 and LG_3 represent suitable leaving groups as defined herein,



(IX)

by reaction with a compound of formula IIIa and IIIb as defined herein, and a compound of formula IIIc

$$HQ^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$$

(IIIc)

wherein R^{13} to R^{18} and Q^3 are as defined for a compound of formula I.

Preferably, in the compounds of formula IIIa, IIIb and IIIc, Q^1 is the same as Q^2 and Q^3, R^1 is the same as R^7 and R^{13}, R^2 is the same as R^8 and R^{14}, R^3 is the same as R^9 and

R^{15}, R^4 is the same as R^{10} and R^{16}, R^5 is the same as R^{11} and R^{17}, and R^6 is the same as R^{12} and R^{18}.

Suitably, LG_3 represents a leaving group as defined herein in respect of LG_1 and LG_2. Preferably, LG_3 represents $NR^{23}R^{24}$ or hydroxyl. Most preferably, LG_3 represents NMe_2, particularly when both LG_1 and LG_2 also represent NMe_2.

Similarly, the compound of formula IX, where LG_3 represents hydroxyl or $NR^{23}R^{24}$, may be prepared by ortho-lithiation of a compound of formula II wherein A_1, A_2, LG_1, LG_2, D, E, M, L_1, L_2, n and m are as defined for a compound of formula II and K represents hydrogen, followed by reaction with a compound of formula Vc

$$A_3{=}LG_3$$

(Vc)

wherein A_3 is as defined for a compound of formula IX and LG_3 represents oxygen or $NR^{23}R^{24}$. Preferably, when employing a compound of formula II to synthesise a compound of formula IX, LG_1 and LG_2 do not represent hydroxyl, as the hydroxyl functionality will typically have to be protected prior to performing the ortho-lithiation reaction. Preferably, both LG_1 and LG_2 represent $NR^{23}R^{24}$, most preferably both LG_1 and LG_2 represent NMe_2.

Similarly, a compound of formula I wherein K is $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and D represents $-A_4-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$ may be prepared from a compound of formula IX wherein A_1, A_2, A_3, LG_1, LG_2, LG_3, E, M, L_1, L_2, n and m are as defined for a compound of

formula IX and D represents hydrogen, by sequential ortho-lithiation and reaction with a compound of formula V(d)

$$A_4=LG_4$$
(Vd)

wherein A_4 is as defined for a compound of formula I and LG_4 represents oxygen or $NR^{23}R^{24}$ as defined herein, to form a compound of formula X followed by reaction of the resultant compound of formula X with a phosphine, arsine or stilbene derivative of formula IIIa, IIIb, IIIc as defined herein and a compound of formula IIId

$$HQ^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$$
(IIId)

wherein R^{31} to R^{36} and Q^4 are as defined for a compound of formula I.

Preferably, in the compounds of formula IIIa, IIIb, IIIc, and IIId, Q^1 is the same as Q^2, Q^3 and Q^4, R^1 is the same as R^7 , R^{13} and R^{31}, R^2 is the same as R^8, R^{14} and R^{32}, R^3 is the same as R^9, R^{15} and R^{33}, R^4 is the same as R^{10}, R^{16} and R^{34}, R^5 is the same as R^{11}, R^{17} and R^{35}, and R^6 is the same as R^{12}, R^{18} and R^{36}.

Suitably, when preparing the 1,2,3,4-substituted derivative of the compound of formula I, preferably LG_1, LG_2 and LG_3 of the compound of formula IX do not represent hydroxyl, but each represents $NR^{23}R^{24}$ as defined herein.

Similarly, a compound of formula I wherein K is $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$, D represents $-A_4-$

$Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$ and E represents $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$ may be prepared from a compound of formula X wherein A_1, A_2, A_3, A_4, LG_1, LG_2, LG_3 and LG_4 , M, L_1, L_2, n and m are as defined for a compound of formula X and E represents hydrogen, by sequential ortho-lithiation and reaction with a compound of formula V(e)

$$A_5{=}LG_5$$

(Ve)

wherein A_5 is as defined for a compound of formula I and LG_5 represents oxygen or $NR^{23}R^{24}$ as defined herein, followed by reaction of the resultant compound with a phosphine, arsine or stilbene derivative of formula IIIa, IIIb, IIIc, IIId and formula IIIe

$$HQ^5(CR^{37}(R^{38})(R^{39})CR^{40}(R^{41})(R^{42})$$

(IIIe)

wherein R^{37} to R^{42} and Q^5 are as defined for a compound of formula I.

Suitably, when preparing the 1,2,3,4,5-substituted derivative of formula I, preferably LG_1, LG_2, LG_3 and LG_4 of the compound of formula X do not represent hydroxyl, but each represents $NR^{23}R^{24}$ as defined herein.

The compounds of formula IIIa, IIIb, IIIc, IIId, IIIe, Va, Vb, Vc, Vd, Ve and VIII and derivatives thereof, when neither commercially available nor subsequently described, may be obtained using conventional synthetic procedures in accordance with standard text books on organic chemistry

or literature precedent, from readily accessible starting materials using appropriate reagents and reaction conditions.

It will be appreciated by those skilled in the art that, within certain of the processes described, the order of the synthetic steps employed may be varied and will depend *inter alia* on factors such as the nature of other functional groups present in a particular substrate, the availability of key intermediates and the protecting group strategy (if any) to be adopted. Clearly, such factors will also influence the choice of reagent for use in the said synthetic steps.

It will also be appreciated that various standard substituents or functional group interconversions and transformations within certain compounds of formula I will provide other compounds of formula I.

According to a fifth aspect, the present invention provides a process for the carbonylation of an ethylenically unsaturated compound comprising contacting an ethylenically unsaturated compound with carbon monoxide and a hydroxyl group containing compound in the presence of a compound of the present invention.

Suitably, the hydroxyl group containing compound includes water or an organic molecule having a hydroxyl functional moiety. Preferably, the organic molecule having a hydroxyl functional group may be branched or linear, and comprises an alkanol, particularly a C_1-C_{30} alkanol, such as neopentyl alcohol, ethylhexyl alcohol, tert-amyl alcohol,

including aryl-alkanols, which may be optionally substituted with one or more substitutents selected from lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29} or $C(O)SR^{30}$ as defined herein. Highly preferred alkanols are C_1-C_8 alkanols such as methanol, ethanol, propanol, iso-propanol, iso-butanol, t-butyl alcohol, n-butanol, octanol, phenol and chlorocapryl alcohol. Although the monoalkanols are most preferred, polyalkanols, preferably, selected from di-octanols such as diols, triols, tetra-ols and sugars are also possible. Typically, such polyalkanols are selected from 1,2-ethanediol, 1,3-propanediol, glycerol, 1,2,4 butanetriol, 2-(hydroxymethyl)-1,3-propanediol, 1,2,6 trihydroxyhexane, pentaerythritol, 1,1,1 tri(hydroxymethyl)ethane, nannose, sorbase, galactose and other sugars. Preferred sugars include sucrose, fructose and glucose. Especially preferred alkanols are methanol and ethanol.

The amount of alcohol is not critical. Generally, amounts are used in excess of the amount of ethylenically unsaturated compound to be carbonylated. Thus the alcohol may serve as the reaction solvent as well, although, if desired, separate solvents may also be used.

It will be appreciated that the end product of the reaction is determined at least in part by the source of hydroxyl group containing compound used. If water is used as the hydroxyl group containing compound then the end product is the corresponding carboxylic acid, whereas use of an alkanol produces the corresponding ester.

Preferably, the ethylenically unsaturated compound includes from 2 to 20 carbon atoms. More preferably, the ethylenically unsaturated compound includes 2 to 14 carbon atoms.

Suitably, the ethylenically unsaturated compound may include more than one carbon-carbon double bond, wherein the double bonds are conjugated or non-conjugated.

Preferably, the ethylenically unsaturated compound has 1 to 3 carbon-carbon double bonds per molecule, particularly 1 to 2 carbon-carbon double bonds, especially only 1 carbon-carbon double bond per molecule.

Unless otherwise specified, the ethylenically unsaturated compound may, when there are a sufficient number of carbon atoms, be linear or branched, be cyclic, acyclic or part cyclic/acyclic, and/or be substituted or terminated by one or more substituents selected from lower alkyl, aryl, alkylaryl, Het, alkylHet, halo, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, NO_2, CN, SR^{27} wherein R^{19} to R^{27} each independently represent hydrogen or lower alkyl olefins thus substituted include styrene and alkyl esters of unsaturated carboxylic acids, such as methacrylate. Suitably, the ethylenically unsaturated compound may exhibit cis (E) and trans (Z) isomerism.

Examples of suitable ethylenically unsaturated compounds having 2 or more carbon atoms include ethene, propene, but-1-ene, but-2-ene, isobutene, pentenes, hexenes, octenes, dodecenes, 1,5-cyclooctadiene, cyclododecene, methyl pentenoate, pentene nitrile, 1,3 butadiene, 1,3

pentadiene and 1,3, hexadiene. A particularly preferred ethylenically unsaturated compound is ethene.

The process according to the invention may be especially advantageous for the carbonylation of ethylenically unsaturated compounds which are internally unsaturated, such as but-2-ene or methyl pent-3-enoate. For these compounds side reactions typically occur more readily and linear products may be more difficult to obtain. Conveniently, the compounds of the invention may permit high regioselectivity towards a linear product following carbonylation of internally unsaturated ethylenic compounds.

Preferably, the carbonylation process is carried out at a temperature of from 0°C to 250°C, more preferably 40°C to 150°C, most preferably 70°C to 120°C.

Suitably, the carbonylation process is typically carried out at a pressure of at least atmospheric pressure. Preferably, the carbonylation process is performed under a total pressure of greater than or equal to $1 \times 10^5 Nm^{-2}$, more preferably greater than or equal to $5 \times 10^5 Nm^{-2}$, most preferably greater than or equal to $10 \times 10^5 Nm^{-2}$. Preferably, the carbonylation process is performed under a total pressure of less than or equal to $100 \times 10^5 Nm^{-2}$, more preferably less than or equal to $65 \times 10^5 Nm^{-2}$, most preferably less than or equal to $50 \times 10^5 Nm^{-2}$.

Carbon monoxide partial pressures in the range of 1 to 65, particularly 5 to 50 $\times 10^5 Nm^{-2}$, are preferred. In the process according to the present invention, the carbon monoxide may be used in pure form or diluted with an inert

gas such as nitrogen, carbon dioxide or a noble gas such as argon. Small amounts of hydrogen, typically less than 5% by volume, may also be present.

The ratio (volume/volume) of ethylenically unsaturated compound to hydroxyl group containing compound may vary between wide limits and suitably lies in the range of 1:0.1 to 1:10, preferably from 2:1 to 1:2.

The amount of the catalyst of the invention used in the carbonylation process of the ethylenically unsaturated compound is not critical. Good results may be obtained by using 10^{-7} to 10^{-1} moles, more preferably 10^{-6} to 10^{-2} moles, of Group VIIIB metal or a compound thereof (referred to as (a) herein) per mole of ethylenically unsaturated compound.

Preferably, as mentioned herein, the compounds of the invention include a source of anions. Suitably, the mole ratio of anions to the moles of Group VIIIB metal in the compounds of the invention when used to carbonylate ethylenically unsaturated compounds lies between wide limits and suitably lies between 2:1 to 2000:1, preferably 5:1 to 500:1, more preferably 10:1 to 200:1.

Suitably, the carbonylation of an ethylenically unsaturated compound as defined herein may be performed in one or more aprotic solvents. Suitable solvents include ketones, such as for example methylbutylketone; ethers, such as for example anisole (methyl phenyl ether), 2,5,8-trioxanonane (diglyme), diethylether, tetrahydrofuran, diphenylether, diisopropylether and the dimethylether of di-ethylene-glycol; esters, such as for example

methylacetate, dimethyladipate and butyrolactone; amides, such as for example dimethylacetamide and N-methylpyrrolidone; and sulfoxides and sulphones, such as for example dimethylsulphoxide, di-isopropylsulphone, sulfolane (tetrahydrothiophene-2,2-dioxide) 2-methylsulfolane and 2-methyl-4-ethylsulfolane.

Very suitable are aprotic solvents having a dielectric constant that is below a value of 50, more preferably in the range of 3 to 8, at 298.15 K and 1 x $10^5 Nm^{-2}$. In the present context, the dielectric constant for a given solvent is used in its normal meaning of representing the ratio of the capacity of a condenser with that substance as dielectric to the capacity of the same condenser with a vacuum for dielectric. Values for the dielectric constants of common organic liquids can be found in general reference books, such as the Handbook of Chemistry and Physics, 76th edition, edited by David R. Lide et al, and published by CRC press in 1995, and are usually quoted for a temperature of about 20°C or 25°C, i.e. about 293.15k or 298.15 K, and atmospheric pressure, i.e. about 1 x $10^5 Nm^{-2}$, or can readily be converted to that temperature and pressure using the conversion factors quoted. If no literature data for a particular compound is available, the dielectric constant may be readily measured using established physico-chemical methods.

For example, the dielectric constant of anisole is 4.3 (at 294.2 K), of diethyl ether is 4.3 (at 293.2 K), of sulfolane is 43.4 (at 303.2 K), of methylpentanoate is 5.0 (at 293.2 K), of diphenylether is 3.7 (at 283.2 K), of dimethyladipate is 6.8 (at 293.2 K), of tetrahydrofuran is

7.5 (at 295.2 K), of methylnonanoate is 3.9 (at 293.2 K). A preferred solvent is anisole.

If the hydroxyl group containing compound is an alkanol, a further preferred aprotic solvent is the ester carbonylation product of the ethylenically unsaturated compound, carbon monoxide and the alkanol.

The process may advantageously be carried out in an excess of aprotic solvent, i.e. at a ratio (v/v) of aprotic solvent to hydroxyl group containing compound of at least 1:1. Preferably, this ratio ranges from 1:1 to 10:1 and more preferably from 1:1 to 5:1. Most preferably the ratio (v/v) ranges from 1.5:1 to 3:1.

The catalyst compounds of the present invention may act as a "heterogeneous" catalyst or a "homogeneous" catalyst.

By the term "homogeneous" catalyst we mean a catalyst, i.e. a compound of the invention, which is not supported but is simply admixed or formed in-situ with the reactants of the carbonylation reaction (e.g. the ethylenically unsaturated compound, the hydroxyl containing compound and carbon monoxide), preferably in a suitable solvent as described herein.

By the term "heterogeneous" catalyst we mean a catalyst, i.e. the compound of the invention, which is carried on a support.

Thus according to a sixth aspect, the present invention provides a catalyst system comprising a support, preferably an insoluble support, and a compound of the

invention as defined herein. Conveniently, the use of an insoluble support permits easy separation of the catalyst, for example by filtration, from the reaction medium.

Preferably, the support comprises a polymer such as a polyolefin, polystyrene and polystyrene/divinylbenezene copolymer; a silicon derivative such as a functionalised silica, a silicone or a silicone rubber; or other porous particulate material such as for example inorganic oxides and inorganic chlorides such as alumina and montmorillomite.

Preferably the support material is porous silica which has a surface area in the range of from 10 to 700 m^2/g, a total pore volume in the range of from 0.1 to 4.0 cc/g and an average particle size in the range of from 10 to 500μm. More preferably, the surface area is in the range of from 50 to 500 m^2/g, the pore volume is in the range of from 0.5 to 2.5 cc/g and the average particle size is in the range of from 20 to 200 μm. Most desirably the surface area is in the range of from 100 to 400 m^2/g, the pore volume is in the range of from 0.8 to 3.0 cc/g and the average particle size is in the range of from 30 to 100 μm. The average pore size of typical porous support materials is in the range of from 10 to 1000 Å. Preferably, a support material is used that has an average pore diameter of from 50 to 500 Å, and most desirably from 75 to 350 Å. It may be particularly desirable to dehydrate the silica at a temperature of from 100°C to 800°C anywhere from 3 to 24 hours.

Suitably, the support may be flexible or a rigid support, the insoluble supported is coated and/or impregnated with

the compound of the invention by techniques well known to those skilled in the art. Alternatively, the compound of the invention is fixed to the surface of insoluble support, optionally via a covalent bond, and optionally includes a bifunctional spacer molecule to space the compound from the insoluble support.

The compounds of the invention may be fixed to the surface of the insoluble support by promoting reaction of a functional group present in the compound of formula I, for example a substituent of the ligand L_1 or a substituent K, D and E of the cyclopentadienyl moiety, with a complimentary reactive group present on or previously inserted into the support. The combination of the reactive group of the support with a complimentary substituent of the compound of the invention provides a heterogeneous catalyst where the compound of the invention and the support are linked via a linkage such as an ether, ester, amide, amine, urea, keto group.

The choice of reaction conditions to link a compound of the present invention to the support depend upon the nature of the substituents(s) of the compound and the groups of the support. For example, reagents such as carbodiimides, 1,1'-carbonyldiimidazole, and processes such as the use of mixed anhydrides, reductive animation may be employed.

According to a seventh aspect, the present invention provides the use of a compound of the invention or a compound of the invention attached to a support as a catalyst.

It will be appreciated that any of the features set forth in the first aspect of the invention may be regarded as preferred features of the second, third, fourth, fifth, sixth and seventh aspect of the present invention and vice versa.

The invention will now be described by way of the following non-limiting examples.

Example 1

Preparation of 1,2-bis-(dimethylaminomethyl)ferrocene

n-Butyllithium (Aldrich, 2.5 molar in hexane, 24 ml, 54 mmol) is added to a solution of (dimethylaminomethyl)ferrocene (Aldrich, 13.13 g, 10.69 ml, 48.97 mmol) in diethyl ether (80 ml) under nitrogen at a temperature of 25°C and the reaction mixture stirred for 4 hours. The resulting red solution is then cooled to approximately -70°C in a dry ice/acetone bath and Eschenmosers salt (ICH_2NMe_2) (Aldrich, 10 g, 54 mmol) is added. The reaction is allowed to warm to room temperature and stirred overnight.

The resultant solution is quenched with excess aqueous sodium hydroxide and the resulting product extracted with diethyl ether (3 x 80 ml) dried over anhydrous magnesium sulfate, filtered over celite, and volatiles removed *in vacuo* to yield the crude title compound as a light orange crystalline solid. The crude product is recrystallised from light petrol with cooling to -17°C and the recrystallised product washed with cold petrol to yield the title compound as a light orange solid (13.2 g, 74%).

The compound can be further purified by sublimation to give 8.5 g (52%) of the title compound (mpt 74°C).

^1H NMR(250 MHz; $CDCl_3$):δ4.23(brd, 2H); 4.11-4.10(t, 1H); 4.04(s, 5H); 3.43, 3.38, 3.23, 3.18 (AB quartet, 2H); 2.22(s, 6H).

^{13}C NMR (63 MHz; $CDCl_3$):δ83.81; 70.40; 69.25; 66.84; 57.35; 45.23.

Elemental analysis:	Found:	C 63.7%;	H 8.9%;	N 9.5%
	Calculated:	C 64.0%;	H 8.1%;	N 9.4%

Example 2

Preparation of 1,2-bis-(ditertbutylphosphinomethyl)ferrocene

Di-tertbutylphosphine (Aldrich, 0.616 ml, 3.33 mmol) was added to a solution of 1,2-bis(dimethylaminomethyl)ferrocene (Example 1, 0.5 g, 1.66 mmol) in anhydrous acetic acid (100 ml) under nitrogen and the resulting mixture is stirred at 80°C for 72 hours. The anhydrous acetic acid is removed *in vacuo* at approximately 70°C to yield the crude title product as an orange/yellow solid. The crude product is recrystallised from ethanol with cooling to -17°C, filtered and the filtrate washed with cold ethanol to yield the title compound as a pale yellow solid (0.365 g, 44%, 84°C).

^1H NMR (250 MHz; $CDCl_3$): δ4.4 (2H, d, J = 2Hz); 3.95(5H, s); 3.75 (1H, t, 2Hz); 2.8 (2H, dd, 12Hz, 2Hz); 2.6 (2H, dd, 12Hz, 2Hz); 1.1 (18H, m).

^{13}C NMR (63 MHz; $CDCl_3$): δ86.73 (d, 5.46 Hz); 70.08 (d, 4.41 Hz); 69.4665(s); 63.75(s); 31.80 (d, 2Hz); 31.45 (d, 1.98Hz); 29.89 (d, 1.88 Hz).

^{31}P NMR (101 MHz; $CDCl_3$): δ15.00 ppm.

Elemental analysis: Found: C:66.79%; H:9.57%
Calculated: C:66.93%; H:9.63%

<u>Example 3</u>

<u>Preparation of 1-hydroxymethyl-2-dimethylaminomethyl ferrocene</u>

n-Butyl lithium (Aldrich, 1.6 molar in diethyl ether, 5.14 ml, 8.24 mmol) is added to a solution of 1-dimethylaminomethyl ferrocene (Aldrich, 1.0g, 4.12mmol) in diethyl ether (20mL) under argon. The reaction is stirred for 3 hours and developes a reddish colour. The solution is then cooled in a dry ice/acetone bath, calcined para-formaldehyde (0.247g, 2 times excess) added and the resultant mixture stirred overnight at room temperature. The reaction is then quenched with water, extracted with diethyl ether, dried over $MgSO_4$, and filtered over celite. The solvent is removed *in vacuo* to yield crude title compound. The crude product is applied to a neutral alumina column, which is eluted with petrol/diethyl ether (9:1 ratio) to remove the starting material, 1-dimethylaminomethyl ferrocene. The column is then eluted with substantially pure ethyl acetate to elute the title compound. The ethyl acetate is removed *in vacuo*, to yield the title compound as an orange oil/crystalline mass.

^{1}H NMR (250 MHz; $CDCl_3$) δ2.131 (s, 6 H), δ2.735 (d, 1 H, 12.512 Hz), δ3.853 (d, 1 H, 12.512 Hz), δ3.984 (dd, 1 H, 2.156 Hz), δ4.035 (s, 5 H), δ4.060 (dd, 1 H, 2.136 Hz) δ4.071 (d, 1 H, 12.207 Hz), δ4.154 (m, 1 H), δ4.73 (d, 1 H, 12.207 Hz).

^{13}C NMR (61 MHz; $CDCl_3$) δ7.688, δ84.519, δ70.615, δ68.871, δ68.447, δ65.369, δ60.077, δ58.318, δ44.414

COSY 2D ^{1}H NMR
Partly obscured doublet at 4.071ppm and its coupling to the doublet at 4.73 ppm confirmed.
Infrared spectra ($CHCl_3$) (c.a. 0.06g / 0.8mL)
2953.8 cm^{-1} , 2860.6 cm^{-1}, 2826.0 cm^{-1}, 2783.4 cm^{-1}, 1104.9 cm^{-1}

Example 4

Preparation of 1,2-bis-(ditertbutylphosphinomethyl)ferrocene

Di-tertbutylphosphine (Aldrich, 0.54 ml, 2.93 mmol) is added to a solution of 1-hydroxymethyl-2-dimethylaminomethyl ferrocene (Example 3, 0.2 g, 0.753 mmol) in anhydrous acetic acid (15 ml) and acetic anhydride (0.753 mmol) under argon and the resulting mixture is stirred at 80°C for 72 hours. The anhydrous acetic acid is removed *in vacuo* at approximately 70°C to yield the crude title product as an orange/yellow solid. The crude product is recrystallised from ethanol with cooling to -17°C, filtered and the filtrate washed with cold ethanol to yield the title compound as an orange solid (0.23 g)

^1H NMR (250 MHz; $CDCl_3$) δ4.351 (d, 2 H, 2Hz), δ4.022 (s, 5 H), δ3.827 (t, 1 H, 2 Hz), δ2.858 (ddd, 2 H, J_{HH} 15.869 Hz, J_{HP1}3.320 Hz, J_{HP2} 1.831 Hz), δ2.679 (dd, 2 H, J_{HH} 15.869 Hz, J_{HP} 2.441 Hz), δ1.166 (d, 18 H, 12.817 Hz), δ1.123 (d, 18 H, 12.512 Hz)

FTIR (Chloroform, NaCl plates)
1104.1 cm^{-1}, 2863cm^{-1}, 2896.0 cm^{-1}, 2940.0 cm^{-1}, 2951.8 cm^{-1}

Elemental analysis: Found: C:66.5%; H:9.6%
Calculated: C:66.9%; H:9.6%

Example 5

Preparation of 1-hydroxymethyl-2,3-bis-(dimethylaminomethyl)ferrocene

To a stirred solution of 1,2-bis-(dimethylaminomethyl) ferrocene (Example 1, 0.70g, 2.32 mmol) in diethyl ether (15 cm^3) under argon is added 1.2 equivalents n-butyl lithium (Aldrich, 1.75mL, 1.6M in diethyl ether) and the mixture stirred for three hours to yield a red solution. The reaction mixture is cooled in a dry ice/acetone bath, calcined paraformaldehyde added in 2:1 excess, and the resultant mixture stirred at room temperature overnight. The mixture is quenched with water and extracted with diethyl ether. The ethereal extracts are dried over $MgSO_4$, filtered over celite and the solvent removed *in vacuo*, to yield the title compound (0.7g , 2.12 mmol, 91%) as an orange oil., which partially crystallized on cooling.

^{1}H NMR (250 MHz; $CDCl_3$) δ 2.133 (s, 6 H), δ 2.171 (s, 6 H), δ 2.910 (d, 1 H, 12.817 Hz), δ 2.998 (d, 1 H, 12.512 Hz), δ 3.425 (d, 1 H, 12.817 Hz), δ 3.812 (d, 1 H, 12.512 Hz), δ 3.962 (s, 5 H), δ 3.99 (d, 1 H, 12.207 Hz) (partly obscured by large cp-ring peak at δ 3.962), δ 4.068 (d, 1 H, δ2.136 Hz), δ 4.125)d, 1 H, δ 2.136 Hz), δ 4.747 (d, 1 H, 12.207 Hz)

^{13}C NMR (60 MHz; $CDCl_3$) δ44.529, δ45.244, δ55.798, δ57.906, δ60.271, δ67.944, δ68.277, δ69.612, δ84.850, δ88.322

Infrared spectra ($CDCl_3$ / thin film NaCl plates) 3380.6 cm^{-1} (br), 2955.7 cm^{-1} (m), 2862.6 cm^{-1} , 2825.9 cm^{-1} (m), 2774.3 cm^{-1} (m), 1353.5 cm^{-1} (m), 1104.9 cm^{-1} (m), 1038.9 cm^{-1} (m), 1006.8 cm^{-1} (s)

Elemental analysis: Found: C: 62.3%; H: 7.8%; N: 8.8%
Calculated: C:61.8%; H:7.9%; N:8.5%

Example 6

Preparation of 1,2,3-tris-(ditertbutylphosphinomethyl)ferrocene

Di-tert-butylphosphine (Aldrich, 2.60 mL, 13.98 mmol) and acetic anhydride (0.24 mL, 2.33 mmol) is added to a solution of 1-hydroxymethyl-2,3-bis-(dimethylaminomethyl)ferrocene (Example 5, 0.70g, 2.12 mmol) in acetic acid (freshly distilled from acetic anhydride 25 cm^3), under argon. The solution is then stirred at 80°C for 7 days, during which time the solution becomes a dark orange colour. The solvent is then removed *in vacuo* and recrystallisation effected from refluxing

ethanol together with cooling to −17°C overnight to yield the title compound (0.43 g, 0.7 mmol, 31%) as a yellow/orange powder.

^1H NMR (250 MHz, $CDCl_3$) δ 1.12 (dd - pseudo triplet, 36 H, 12.1 Hz), δ1.26 (d, 18H, 10.7 Hz), δ2.68 (d, 2 H, 17.7 Hz), δ2.95 (s, 2 H), δ3.07, (m, 2 H), δ4.01 (s, 5 H) δ 4.33 (s, 2 H)

Infrared spectra ($CHCl_3$ / thin film NaCl plates) 1365.5 cm^{-1}, 1470.3 cm^{-1} , 2357.1 cm^{-1} ,2862.8 cm^{-1} , 2896.7 cm^{-1} , 2939.1 cm^{-1}

Example 7

Preparation of methyl propanoate from ethylene, carbon monoxide and methanol

A mechanically stirred autoclave of 2 litre capacity was evacuated of air and then charged with a solution of tri(dibenzylideneacetone)dipalladium (1.44 x 10^{-5} moles) and 1,2-bis-(di-tertbutylphosphinomethyl)ferrocene of Example 2, (7.61 x 10^{-5} moles) in 300 ml of methyl propanoate/methanol (70 wt% methyl propanoate). The autoclave was heated to 100°C and when at that temperature, ethylene (8 x $10^5 Nm^{-2}$) was added on top of the vapour pressure of the solvents and immediately an equimolar mixture of carbon monoxide and ethylene (2 x $10^5 Nm^{-2}$) added to the system through a pressure regulating valve set to 10 x $10^5 Nm^{-2}$ above the solvent vapour pressure. Suitably, the molar ratio of ethylene to carbon monoxide in the reactor is approximately 9:1. The

temperature of the reactor was maintained at 100°C and as the reaction proceeded additional carbon monoxide and ethylene was added (on an equimolar basis) through the pressure regulating Tescom valve. No catalyst precipitation was observed.

Initial reaction rates measured in moles of methyl propanoate (MeP) per mole of palladium per hour and turnover measured in moles of methyl propanoate per mole of palladium were determined for the catalyst. This may be accomplished by an analysis of the amount of gas consumed per unit time (rate) and the total amount of gas consumed during the reaction, assuming ideal gas behaviour and 100% selectivity to methyl propanoate.

The reaction was repeated (Run 2) and initial reaction rates and turnover numbers calculated as described above. The data for both runs is displayed in Table 1.

	Maximum (moles MeP/mole Pd/hr) Initial Rate	Turnover (moles MeP/mole Pd/hr) number after 3 hours
Run 1	31,810	59,941
Run 2	30,322	63,941

Table 1

Comparative Example 8

Preparation of methyl propanoate from ethylene, carbon monoxide and methanol

Example 3 was repeated twice (Runs 3 and 4 respectively) except the catalyst system was as disclosed in WO 96/19434 and obtained by charging the autoclave with tri(debenzylideneacetone)dipalladium (1.44 x 10^{-5} moles), 1,2 bis(di-t-butylphosphinomethyl)benzene (7.61 x 10^{-5} moles) in methyl propanoate/methanol (300 ml, 70 wt% methyl propanoate).

The initial reaction rates (moles MeP/mole Pd per hour) and turnover numbers (moles Pd/moles MeP) for the catalyst were calculated as described in Example 3 above. The results are presented in Table 2 below.

	Maximum Initial Rate (moles Pd/moles MeP/hr)	Turnover number after 3 hours (moles Pd/mole MeP)
Run 3	29,730	48,386
Run 4	30,335	51,997

Table 2

The results demonstrate (see Table 1 and Table 2), that the catalyst of the present invention (palladium 1,2-bis-(di-t-butylphosphinomethyl)ferrocene and the known palladium 1,2-bis(di-t-butylphosphinomethyl)benzene exhibit comparable initial catalytic reaction rates. However, the turnover number for the catalyst of the invention is significantly higher than that for the known palladium 1,2-bis(di-t-butylphosphinomethyl)benzene catalyst, thereby indicating that the compound of the

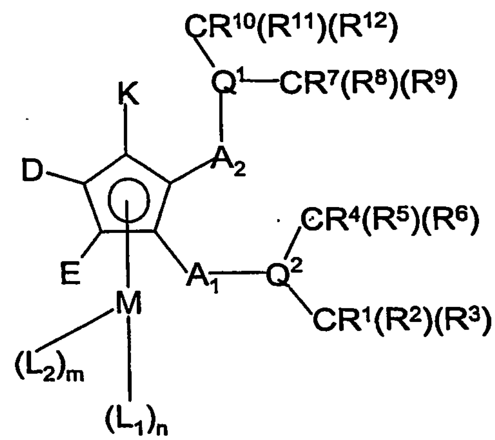
present invention increases the rate of the carbonylation reaction compared to the known bidentate system.

Claims

1. A compound obtainable by combining:

(a) a Group VIIIB metal or a compound thereof; and,

(b) a compound of formula I



(I)

wherein:

A_1 and A_2, and A_3, A_4 and A_5 (when present), each independently represent lower alkylene;

K is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29}, $C(O)SR^{30}$, or $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$;

D is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29}, $C(O)SR^{30}$, or $-A_4-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$;

E is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29}, $C(O)SR^{30}$, or $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$;

or both D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form a phenyl ring, which is optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29} or $C(O)SR^{30}$;

R^1 to R^{18} and R^{31} to R^{42} each independently represent lower alkyl, aryl, or Het;

Q^1 and Q^2, and Q^3, Q^4 and Q^5 (when present), each independently represent phosphorus, arsenic or antimony;

M represents a Group VIB or VIIIB metal or metal cation thereof;

L_1 represents a cyclopentadienyl, indenyl or aryl group each of which groups are optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{27}R^{28}$, SR^{29}, $C(O)SR^{30}$ or ferrocenyl;

L_2 represents one or more ligands each of which are independently selected from hydrogen, lower alkyl, alkylaryl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$;

R^{19} to R^{30} and R^{43} to R^{48} each independently represent hydrogen, lower alkyl, aryl or Het;

$n = 0$ or 1;

and $m = 0$ to 5;

provided that when $n = 1$ then m equals 0, and when n equals 0 then m does not equal 0;

provided that when both K represents $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and E represents $-A_5-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$, then D represents $-A_4-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$.

2. A compound as claimed in claim 1 wherein each of Q^1 and Q^2, and Q^3, Q^4 and Q^5, (when present), are the same, preferably phosphorus.

3. A compound as claimed in claims 1 or 2 which is obtainable by combining: (a) palladium or a compound thereof; and (b) a compound of formula I.

4. A compound as claimed in anyone of the preceding claims wherein R^1 to R^{18} and R^{31} to R^{42} each independently represent C_1 to C_6 alkyl, C_1-C_6 alkylphenyl or phenyl, preferably non-substituted C_1 to C_6 alkyl.

5. A compound as claimed in any one of claims 1 to 4 wherein each of R^1, R^4, R^7 and R^{10}, and R^{13}, R^{16}, R^{31}, R^{34}, R^{37} and R^{40} (when present) is identical.

6. A compound as claimed in any one of the preceding claims wherein each of R^2, R^5, R^8 and R^{11}, and R^{14}, R^{17}, R^{32}, R^{35}, R^{38} and R^{41} (when present) is identical.

7. A compound as claimed in any one of the preceding claims wherein each of R^3, R^6, R^9 and R^{12}, and R^{15}, R^{18}, R^{33}, R^{36}, R^{39} and R^{42} (when present) is identical.

8. A compound as claimed in any one of the preceding claims wherein each of R^1 to R^{12}, and R^{13} to R^{18} and R^{31} to R^{42} (when present), is identical, particularly methyl.

9. A compound as claimed in any one of claims 1 to 3 wherein each of the groups selected from the groups R^1 to R^3, R^4 to R^6, R^7 to R^9, R^{10} to R^{12}, R^{13} to R^{15}, R^{16} to R^{18}, R^{31} to R^{33}, R^{34} to R^{36}, R^{37} to R^{39} or R^{40} to R^{42} together independently form a cyclic structure.

10. A compound as claimed in anyone of the preceding claims wherein A_1 and A_2, and A_3, A_4 and A_5 (when present), each independently represent C_1 to C_6 alkylene.

11. A compound as claimed in anyone of the preceding claims wherein each of A_1 and A_2, and A_3, A_4 and A_5 (when present), are identical and represent C_1 to C_6 alkylene, preferably methylene.

12. A compound as claimed in anyone of the preceding claims wherein D and E independently represent hydrogen or C_1-C_6 alkyl.

13. A compound as claimed in anyone of the preceding claims wherein D and E are identical.

14. A compound as claimed in anyone of the preceding claims wherein D, E and K are identical.

15. A compound as claimed in anyone of claims 1 to 11 wherein D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form a phenyl ring, and the phenyl ring is optionally substituted with one or more substituents selected from lower alkyl, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$ or $C(O)NR^{25}R^{26}$.

16. A compound as claimed in claim 15 wherein D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring.

17. A compound as claimed in anyone of the preceding claims wherein K represents hydrogen or C_1-C_6 alkyl, preferably hydrogen.

18. A compound as claimed in anyone of claims 1 to 13, 15 or 16 wherein K represents $-A_3-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$, preferably $-CH_2-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$.

19. A compound as claimed in claim 18, wherein D represents $-A_4-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$, preferably $-CH_2-Q^4(CR^{31}(R^{32})(R^{33}))CR^{34}(R^{35})(R^{36})$.

20. A compound as claimed in claim 19, wherein E represents $-CH_2-Q^5(CR^{37}(R^{38})(R^{39}))CR^{40}(R^{41})(R^{42})$.

21. A compound as claimed in anyone of the preceding claims wherein M represents Cr, Fe, Co, Mo or Ru or a metal cation thereof.

22. A compound as claimed in claim 21 wherein M represents iron or a cation thereof.

23. A compound as claimed in anyone of the preceding claims wherein L_1 represents cyclopentadienyl, indenyl, phenyl or napthyl, preferably cyclopentadienyl.

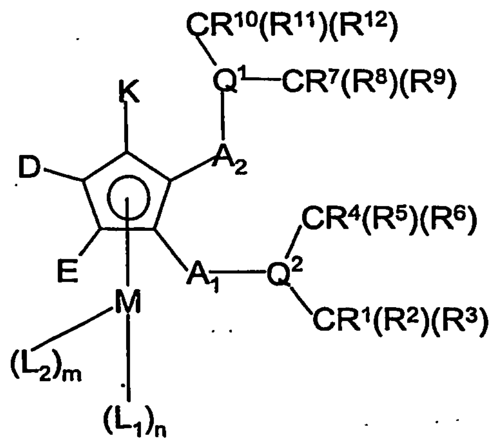
24. A compound as claimed in anyone of the preceding claims wherein L_2 represents one or more ligands each of which ligands are independently selected from C_1 to C_4 alkyl, chloro, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$.

25. A compound as claimed in anyone of the preceding claims wherein n=1 and m=0.

26. A compound as claimed in any one of the preceding claims wherein n = 0 and m = 3 or 4, preferably 3.

27. A process for preparing a compound as defined in any one of claims 1 to 26 comprising combining (a) a Group VIIIB metal or compound thereof; and, (b) a compound of formula I as defined in any one of claims 1 to 26.

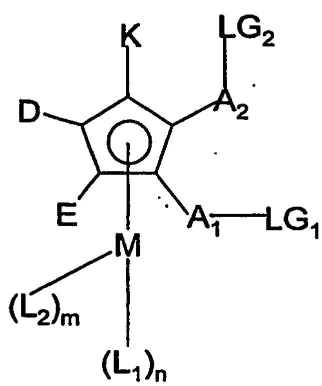
28. A compound of formula I



(I)

wherein A_1, A_2, K, D, E, M, L_2, L_1, Q^1, Q^2, R^1 to R^{12}, n and m are as defined in any one of claims 1 to 26.

29. A process for preparing a compound of formula I as defined in any one of the preceding claims, comprising reacting a compound of formula II wherein A_1, A_2, K, D, E, M, L_1, L_2, n and m are as defined for a compound of



(II)

formula I, and LG_1 and LG_2 represent suitable leaving groups, with a compound of formula IIIa and IIIb

$HQ^2(CR^1(R^2)(R^3))CR^4(R^5)(R^6)$
(IIIa)

$HQ^1(CR^7(R^8)(R^9))CR^{10}(R^{11})(R^{12})$
(IIIb)

wherein R^1 to R^{12}, Q^1 and Q^2 are as defined for a compound of formula I.

30. A compound of formula II as defined in claim 29.

31. A process for the carbonylation of an ethylenically unsaturated compound comprising contacting an ethylenically unsaturated compound with carbon monoxide and a hydroxyl group containing compound in the presence of a compound as defined in any one of claims 1 to 27.

32. A process as claimed in claim 31 wherein the ethylenically unsaturated compound comprises ethylene.

33. A composition comprising a compound as defined in any one of claims 1 to 27 attached to a support.

34. Use of a compound as defined in anyone of claims 1 to 27 or a composition as defined in claim 33 as a catalyst.

ABSTRACT

A catalyst suitable for carbonylating ethylenically unsaturated compounds comprising a Group VIIIB metal or compound thereof and a metallocene.